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SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT		ATTORNEY DOCKET NO.
09/730,684	12/06/00	JONES	M	

07M1/0808

PRATT & WHITNEY
PATENT DEPARTMENT
MAIL STOP 132-13
400 MAIN STREET
EAST HARTFORD CT 06108

EXAMINER	
MILLER, E	
ART UNIT	PAPER NO.
3641	

DATE MAILED: 08/08/01

PETITION NO.: 13,109

To: Secretary, ~~ASPAB~~ Air force

The attached copy of a petition for modification or rescission of the Secrecy Order(s) is forwarded for recommendation by your office. In order to assure a timely response to the patent applicant on their petition, please respond within 30 DAYS of the above mail date.

Enclosures as indicated:

Application

Exhibit

Katie Osborne
KATIE OSBORNE
Licensing and Review
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of

Marvin Luther Jones et al. Docket No.: D-1460

Serial No.: 09/730,684 Examiner: E. Miller

Filing Date: 6 December 2000 Art Unit: 3641

Title: SOLID ROCKET PROPELLANT

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Commissioner of Patents and Trademarks
Washington, DC 20231

13/09

PETITION FOR RECISSION OF SECRECY ORDER UNDER 37 C.F.R. § 5.4

Sir:

The Applicants respectfully petition for the Secrecy Order imposed on 7 July 2001 (copy attached) to be rescinded on the grounds that the order is ineffectual and/or futile. The Applicants offer the following facts:

1. The present application, Serial No. 09/730,684 filed on 6 December 2001, is a divisional of a previously co-pending application, Serial No. 09/356,175 filed on 16 July 1999.

2. The parent of the present application, which contains the identical disclosure as the present application, issued as US Patent 6,238,499 on 29 May 2001 (copy attached)—almost two months before the secrecy order was imposed on the present application.

3. The Applicants filed foreign patent applications based on the parent of the present application in the European Patent Office (application 00305886.4, filed 12 July 2000) and in the Japanese Patent Office (application 2000-213748, filed 14 July 2000). The European patent application, which contains the identical disclosure as the present application, was published on 17 January 2001 as EP 1 069 095 A1 (copy attached).

4. The present application is not related to a contract between the Government and any of the principals.

Because of issuance of US Patent 6,238,499 and publication of European Patent Application EP 1 069 095 A1, both of which have disclosures identical to that of the present application, before the imposition of the Secrecy Order, the Applicants respectfully assert that the Secrecy Order is ineffectual and/or futile to prevent public disclosure of the contents of the present application. Therefore, the Applicants ask that the Secrecy Order be rescinded.

Respectfully submitted,

MARVIN LUTHER JONES ET AL.

By: George J. Romanik
Attorney of Record
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3 August 2001

UNITED STATES DEPARTMENT OF COMMERCE
Patent and Trademark Office
ASSISTANT SECRETARY AND COMMISSIONER
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SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
09/730,684	12/06/00	JONES	

EXAMINER ~~D-1460~~

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PRATT & WHITNEY
PATENT DEPARTMENT
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07/19/01

SECRECY ORDER
35 U.S.C. §§181-188

Including:
Permit for Disclosing Subject Matter to Government Employees and Other Specified Persons ("Permit A")

The above-identified patent application contains subject matter the unauthorized disclosure of which would, in the opinion of the sponsoring defense agency be detrimental to the national security.

ALL PRINCIPALS[1] IN THIS APPLICATION ARE ORDERED TO KEEP THE SUBJECT MATTER THEREOF IN SECRECY UNDER 35 U.S.C. §181.

The subject matter of this application may not be published or disclosed to any person except as specifically authorized herein or subsequently authorized by written modification of this Secrecy Order granted by the Commissioner of Patents & Tramemarks (see 37 CFR §5.5).

Unauthorized publication or disclosure of the subject matter of this patent application may result in abandonment of the application (35 U.S.C. §182) and additionally subject the person publishing or disclosing the subject matter to the penalties of 35 U.S.C. §186.

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[1] "Principals" include all patent applicants, their heirs, assignees, licensees and their attorneys and agents.

The subject matter of this application must be safeguarded under conditions that will provide adequate protection and prevent access by unauthorized persons. When copies of the subject matter are no longer needed, they should be destroyed by a method that will prevent disclosure of the contents or reconstruction of the document.

The subject matter of this application may not be disclosed to any person except as authorized herein without written modification of this Secrecy Order by the Commissioner of Patents & Trademarks.

Any other patent application already or hereafter filed in the U.S. or any foreign country which contains any significant part of the subject matter of the above-identified patent application also falls within the scope of this Order. If such other patent application is not currently under a Secrecy Order imposed by the U.S. Patent and Trademark Office, it and the common subject matter must be brought to the immediate attention of:

Director, Special Laws Administration
Attention: Licensing and Review
U.S. Patent and Trademark Office
Washington, D.C. 20231.

This Order should not be construed in any way to mean that the U.S. Government has adopted or contemplates adoption of the invention disclosed in this application and it is not any indication of the value of such invention. Additionally, this Order is not an indication in and of itself that the subject matter of this application is or should be classified.

This Secrecy Order was recommended to the Commissioner of Patents & Trademarks by the following sponsoring defense agency:

( ) ARMY ( ) NAVY (X) AIR FORCE

Questions regarding the reasons for imposing this Secrecy Order should be directed to the sponsoring defense agency. A contact for each defense agency is attached. Questions regarding the substantive examination of the patent application should be directed to the patent examiner, and questions pertaining to the administrative handling of the application or the Secrecy Order should be directed to the Licensing and Review Branch of the Patent & Trademark Office.

Permit for Disclosing to Government Employees and Other Specified Persons ("Permit A")

The principals designated in this Order are authorized to disclose the subject matter to any person of the classes hereafter specified if such person is known to the principal disclosing to

be concerned directly in an official capacity with the subject matter, provided that all reasonable safeguards are taken to otherwise protect the invention from unauthorized disclosure. The specified classes are:

a. any officer or employee of any department, independent agency or bureau of the Government of the United States; or
b. any person designated specifically by the head of any department, independent agency or bureau of the Government of the United States, or by his duly authorized subordinate, as a proper individual to receive the subject matter.

Principals under this Order are further authorized to disclose the subject matter of this application to the minimum necessary number of persons of known loyalty and discretion, employed by or working with the principals or their licensees and whose duties involve cooperation in the development, manufacture or use of the subject matter by or for the Government of the United States, provided such persons are advised of the issuance of this Order.

The provisions of this permit do not in any way lessen responsibility for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and national security.

~~John~~ F. Terapane
Director, Special Laws Administration

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(12) **United States Patent**
Jones et al.

(10) **Patent No.:** **US 6,238,499 B1**
(45) **Date of Patent:** **May 29, 2001**

(54) **SOLID ROCKET PROPELLANT**

(75) Inventors: **Marvin Luther Jones**, Hollister; **Donald Dongjaw Tzeng**, San Jose, both of CA (US)

(73) Assignee: **United Technologies Corporation**, Hartford, CT (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/356,175**

(22) Filed: **Jul. 16, 1999**

(51) **Int. Cl.**^{7} **C06B 45/10**; C08G 63/78

(52) **U.S. Cl.** **149/19.4**; 149/19.1; 149/19.6; 528/279

(58) **Field of Search** 149/19.4, 19.6, 149/19.1

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* cited by examiner

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(57) **ABSTRACT**

A solid rocket propellant includes a binder that is a linear block co-polymer of caprolatone and tetramethylene ether and an oxidizer. The propellant may be disposed of by contacting it with an aqueous solution of 12 N NaOH or 6 N HCl at a temperature of about 140° F. for about 24 hours to decompose the binder. Solids remaining in the solution after the binder decomposes are removed.

11 Claims, No Drawings

SOLID ROCKET PROPELLANT

TECHNICAL FIELD

The present invention is directed to a solid rocket propellant.

BACKGROUND ART

Solid rocket propellants typically comprise an oxidizer, a fuel, a variety of additives, and a binder that holds the propellant together. Typical oxidizers include ammonium nitrate, ammonium dinitramide, ammonium perchlorate, potassium perchlorate, and other compounds known in the art. Typical fuels include aluminum powder, boron, and beryllium. Typical binders include nitrocellulose, hydroxy terminated polybutadiene, butadiene terpolymer, polybutadiene-acrylic acid-acrylonitrile, carboxyl terminated polybutyidiene, polyesters, polyethylene glycol, poly tetramethylene glycol and other compounds known in the art. Typical additives include plasticizers such as n-butyl nitratoethyl nitramine, trimethylolethane trinitrate and isodecyl pelargonate, dioctyl adipate; burning rate modifiers such as iron oxide and carbon; combustion stabilizers such as zirconium oxide; anti-oxidants such as n-methyl nitroaniline and 2,2'-Methylene-Bis-(4-Methyl6-Tert-Butylphenol) (available as AO-2246 from American Cyanamid Company, Parsippany, NJ); curing agents such as dimeryl diisocyante, isophorone diisocyanate, and Desmodur® N-100 (available from Bayer Corporation, Pittsburgh, PA); curing catalysts such as triphenyl bismuth and dibutyltin dilaurate; and acoustic suppressants such as silicon carbide.

Solid rocket propellants can be tailored to specific applications by varying their formulations. Although preliminary work on new formulations can be done in a laboratory with small quantities, testing and large scale demonstrations are typically required before a new formulation is accepted for military or commercial use. As a result, propellant development programs often generate considerable excess inventory of propellant. Production programs also generate excess inventory or off specification material. Finally, excess propellant is generated when rocket motors are periodically remanufactured to replace aging propellant with fresh propellant. In all cases, the excess inventory or off-specification material must be disposed of safely. Historically, open air incineration was the preferred disposal method. Increasingly, however, open air incineration is becoming environmentally unacceptable. Therefore, what is needed in the industry is a solid rocket propellant that can be disposed of with environmentally acceptable techniques.

DISCLOSURE OF THE INVENTION

The present invention is directed towards a solid rocket propellant that can be disposed of with environmentally acceptable techniques. As a side benefit, main components of the propellant can be recovered for reuse.

One aspect of the invention includes a solid rocket propellant that includes a hydroxy-terminated caprolactone ether binder.

Another aspect of the invention includes a method of disposing of a solid rocket propellant. A solid rocket propellant that includes a hydroxy-terminated caprolactone ether binder and one or more solid compounds disposed in the binder is contacted with a solution capable of hydrolyzing the binder to binder to form hydrolyzed caprolactone and poly(tetramethylene ether),. Solids remaining in the solution after the binder hydrolyzes are removed.

These and other features and advantages of the present invention will become more apparent from the following description.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention includes a full range of solid rocket propellant formulations, including minimum smoke propellants, reduced smoke propellants, and metalized propellants. The common element in all aspects of the present invention is the use of a hydroxy-terminated caprolactone ether (HTCE) polymer as a binder to hold the solid constituents of the propellant of the present invention together. As a result, the propellant of the present invention comprises at least one solid compound, for example an oxidizer, dispersed in an HTCE binder. For purposes of this application, HTCE is a linear block co-polymer of caprolactone and tetramethylene ether. Preferably, HTCE will have a molecular weight of about 2000 units to about 4200 units. At typical HTCE may have an OH value of about 56 mg KOH/g, an acid value of less than about 0.1 mg KOH/g, and a melting range of about 86° F. to about 95° F. The preferred HTCE is a waxy solid at room temperature and is a liquid at typical propellant processing temperatures of 120° F. to 140° F. HTCE is commercially available from Solvay Interox, Inc. (Houston TX) as part of Solvay's CAPA® line of polycaprolactones. The HTCE binder may make up about 4 weight % to about 10 weight % of the propellant of the present invention.

Minimum smoke propellants of the present invention include an HTCE binder and a chlorine-free oxidizer. Suitable chlorine-free oxidizers include ammonium nitrate (AN), ammonium dinitramide (ADN), nitramines such as cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX), and other chlorine-free oxidizers known in the art. A minimum smoke propellant may comprise about 45 weight % to about 75 weight % of the oxidizer. If desired, the propellant also may include one or more nitrate ester plasticizers such as n-butyl nitratoethyl nitramine (BuNENA), trimethylol ethane trinitrate (TMETN), triethylene glycol dinitrate (TEGDN), and other nitrate ester plasticizers known in the art for additional energy. Plasticizers may make up about 6 weight % to about 18 weight % the minimum smoke propellant. Minimum smoke propellants of the present invention may have a theoretical specific impulse of more than 230 lb_f sec/lb_m with an AN oxidizer and more than 260 lb_f sec/lb_m with an ADN oxidizer. Such propellants may be useful in tactical applications where a visible exhaust is undesirable because it would expose a rocket's firing position.

Reduced smoke propellants of the present invention include an HTCE binder and a chlorinated oxidizer. Suitable chlorinated oxidizers include ammonium perchlorate (AP), which may make up about 65 weight % to about 86 weight % of a reduced smoke propellant. If desired, the propellant also may include one or more energetic plasticizers such as BUNENA, TMETN, and TEGDN or fuel plasticizers such as dioctyl adipate (DOA) or isodecyl pelargonate (IDP). Plasticizers may make up about 5 weight % to about 12 weight % of the reduced smoke propellant. Reduced smoke propellants of the present invention may have a theoretical specific impulse of more than 244 lb_f sec/lb_m with an AP oxidizer. Such propellants may be useful in tactical applications, such a air-to-air applications, where a small amount of visible exhaust is tolerable as long as the exhaust does not obscure an operator's field of view.

Metalized propellants of the present invention include an HTCE binder, metal fuel, and an oxidizer. Suitable metal

fuels include aluminum, boron, and other metal fuels known in the art. The preferred metal fuel is aluminum. The metal fuel may make up about 15 weight % to about 24 weight % of the metalized propellant. Suitable oxidizers include AP, AN, ADN, HMX, RDX, and other oxidizers known in the art. The oxidizer may make up about 45 weight % to about 75 weight % of the metalized propellant. If desired, the propellant also may include one or more energetic plasticizers, such as TMETN or TDGDN, or fuel plasticizers, such as DOA or IDP. Plasticizers may make up about 5 weight % to about 12 weight % of metalized propellants of the present invention. Metalized propellants of the present invention may have a theoretical specific impulse of more 263 lb_f sec/lb_m with AP oxidizer and 268 lb_f sec/lb_m with ADN or HMX oxidizer. Such propellants may be useful in applications for which high energy content is desirable and for which visible exhaust is not a problem.

The HTCE binder of the present invention can be cured with a variety of curing agents including di-functional isocyanates such as isophorene diisocyante (IPDI), dimeryl diisocyanate (DDI), bis-(4,isocyanatocyclohexyl) methane (Desmodur®-W, available from Bayer Corporation, Pittsburgh, PA), and other di-functional isocyanates; and poly-functional isocyanates such as aliphatic isocyanates made by the homo-polymerization of hexamethylene diisocyanate, including Desmodur® N-100 and Desmodur® N-3200 (both available from Bayer Corporation), and other poly-functional isocyanates. The curing agent may make up as much as about 2.75 weight % of the propellant. A cross-linker may be desirable when di-functional isocyanates are use as curing agents. Preferable cross-linkers include tri-functional and tetra-functional hydroxy terminated caprolactones, such as CAPA® 310 and CAPA® 316 (available from Solvay Interox, Inc.). The cross-linker may make up as much as about 2.0 weight % of the propellant of the present invention. A cure catalyst such as triphenyl bismuth (TPB), dibutyltin dilaurate (DBTDL), or similar cure catalysts may be used to speed the cure reaction. Typical amounts of TPB in the propellant range from about 0.01 weight % to about 0.05 weight %. Typical amounts of DBTDL range from about 1 PPM by weight to about 6 PPM by weight. HTCE may be cured under conditions typically used in the industry. For example, HTCE may be cured at temperatures of about 120° F. to about 140° F. for times ranging from 3 days to 2 weeks.

The propellant of the present invention also may include stabilizers, acoustic suppressants, burner rate modifiers, and other additives. For example, propellants of the present invention may include up to about 0.5 weight % of one or more stabilizers, such as N-methyl-p-nitroanaline (NMNA), 2-nitro diphenylamine (NDPA), or other stabilizers known in the art, to extend their useful lives. Stabilizers may be particularly useful in propellants that contain nitrate ester plasticizers. The propellants also may include up to about 0.5 weight % of an acoustic suppressants such as silicon carbide or zirconium carbide. Burn rate modifiers, such as carbon black and/or lead compounds including lead citrate, may be included in the propellant of the present invention in amounts up to about 0.2 weight %. Iron oxide can be used as a burning rate modifier in formulations without energetic nitrate ester plasticizers in amounts up to about 2 weight %.

By varying the formulation, bum rates for the propellant of the present invention may be tailored for numerous applications. Burning rates have been observed as low as 0.18 in/sec and as high as 0.34 in/sec at 1000 psi for formulations without any burning rate modifiers. Pressure exponents were between 0.3 and 0.4. The ranges of burning rates and pressure exponents may be expanded by using various additives and curing catalysts discussed above. It should be possible to formulate metalized propellants with iron oxide burning rate catalyst that have burning rates as high as 0.75 inisec at 1000 psi.

The mechanical properties of the HTCE binder, such as modulus, tensile strength, and elongation, also may be tailored for particular applications. For example, the modulus may be varied from about 300 psi to about 700 psi, the tensile strength may be varied from about 75 psi to about 150 psi, and the elongation may be varied from about 30% to about 150% of the propellant of the present invention. One way to adjust the mechanical properties of the binder is to vary the isocyanate/hydroxyl (NCO/OH) equivalent ratio. For example, the NCO/OH equivalent ratio may be varied from about 0.95 to about 1.20. Another method is to add about 0.1 weight % to about 2.0 weight % of a tri-functional or tetra-functional hydroxyl-terminated caprolactone to the formulation as a cross-linker in the propellant. The cross-linker promotes cross-linking within the HTCE co-polymer structure. Suitable cross-linkers include tri-functional and tetra-functional hydroxy terminated caprolactones, such as CAPA® 310 and CAPA® 316 (available from Solvay Interox, Inc.).

Once a specific formulation is chosen, the ingredients are mixed in an explosion proof mixing vessel according to industry practices to create an uncured propellant. The uncured propellant may be loaded into a rocket casing or other container by known casting techniques and cured under suitable conditions. For example, the propellant of the present invention may be cured at temperatures of about 120° F. to about 140° F. It may take about 3 days to about 14 days to cure a batch of propellant of the present invention. Samples of the cured propellant may then be tested to confirm the properties. The final product would then be ready to deliver to the customer.

Over time, quantities of propellant that require disposal may be accumulated as a result of off-specification mixing, excess production, natural degradation of the propellant, obsolescent propellant or missiles being removed from service, and similar events. In the past, such propellant was typically disposed of by open air incineration. Propellants of the present invention, however, may be disposed of by hydrolyzing the HTCE binders in the propellant. The ester linkage in the caprolactone in the HTCE binder provides the site for hydrolysis. The polyether linkage in the HTCE binders increase the hydrophilicity of the cured binder toward aqueous acidic andlor basic solutions. Thus, the polyether linkage is more resistant to hydrolysis that the ester linkage.

To dispose of propellant of the present invention by hydrolysis, the propellant may be reduced in size to facilitate handing and increase surface area for the reaction. While no particular size reduction is required, preferably the propellant will be reduced to pieces of no more than about 0.5 inch in any dimension. The propellant is then mixed with a solution capable of hydrolyzing HTCE. For example, HTCE may be hydrolized in an acidic aqueous solution of 6 N HCl (hydrochloric acid) or a basic aqueous solution of 12 N NaOH (sodium hydroxide). One skilled in the art will recognize that solutions with different compositions and concentrations would work as well. Preferable, the hydrolysis will be conducted at an elevated temperature, for example about 140° F., for a sufficient time to completely hydrolyze the HTCE. Agitation can speed the hydrolysis reaction. By selecting appropriate conditions, hydrolysis can be completed within about 24 hours. As a result of the

hydrolysis reaction, the HTCE binder will decompose into water soluble, environmentally benign compounds such as hydrolyzed caprolactone, typically ω-hydroxyl caproic acid, and poly(tetramethylene ether) that may be recycled. Solids that were in the propellant, for example the oxidizer and other solids, may be recovered and recycled for use in other propellants. Aluminum may be recovered as aluminum oxide. The ability to recover and reuse the solids, which may make up 85 weight % or more of the propellant, greatly reduces the environmental impact of disposing of propellants of the present invention. The residue of hydrolysis that cannot be recycled may be disposed of in a suitable landfill without any environmental harm.

The following examples demonstrates the present invention without limiting the invention's broad scope.

EXAMPLE 1

To demonstrate the present invention, several propellants were formulated using a HTCE binder. The table shows the compositions, mechanical properties, and where available burning rate and pressure exponent data.

TABLE

	Propellant A Metalized	Propellant B Metalized	Propellant C Reduced Smoke
HTCE binder (MW = 2000)	8.80	4.21	6.21
CAPA ® 316 cross-linking agent	0.18	1.05	1.04
Diocytal adipate (DOA) plasticizer	4.84		
n-butyl nitratoethyl nitramine (BuNENA) plasticizer		15.54	10.65
n-methyl nitroanaline (NMNA) stabilizer		0.50	0.50
triphenyl bismuth (TPB) cure catalyst	0.05	0.05	0.05
silicon carbine (SiC) acoustic suppressant			0.50
carbon (C) black burning rate modifier			0.20
dimeryl diisocyante (DDI) curing agent	3.13	2.50	3.40
ammonium perchlorate (AP) oxidizer	63.00	56.00	77.20
aluminum (Al) fuel	20.00	20.00	
modulus, psi	623	100	383
tensile strength, psi	92	29	45
elongation, failure %	65	43	20
burning rate, in/sec @ 1000 psi		0.28	0.26
pressure exponent		0.39	0.36

EXAMPLE 2

A 2.0-gram sample of cured HTCE gum stock was cut into small pieces of no more than 0.5 inch in any dimension. The cut pieces were placed in a beaker containing 50-ml of 12 N NaOH aqueous solution. The solution was stirred with a magnetic stirrer and heated on a hot plate. The reaction temperature was kept at 60° C. At the end of reaction, about 24 hours, all solid gum stock dissolved and some oil droplet suspension was visible. These results indicate that the HTCE binder may be hydrolyzed as part of a method of disposing of a propellant of the present invention.

The invention is not limited to the particular embodiments shown and described herein. Various changes and modifications may be made without departing from the spirit or scope of the claimed invention.

We claim:

1. A rocket motor propellant comprising a binder that is a linear block co-polymer of caprolactone and tetramethylene ether and an oxidizer.

2. The propellant of claim 1, wherein the linear block co-polymer of caprolactone and tetramethvlene ether has a molecular weight of about 2000 to about 4200 units.

3. The propellant of claim 1, wherein the oxidizer comprises ammonium nitrate, ammonium dinitramide, cyclotrimethylene trinitramide, or cyclotetramethylene tetranitramine.

4. The propellant of claim 1, further comprising a plasticizer that comprises n-butyl nitratoethyl nitramine, trimethylol ethane trinitrate, or triethyleneglycol dinitrate.

5. The propellant of claim 1, wherein the oxidizer comprises ammonium nitrate, ammonium dinitramide, cyclotrimethylene trinitramide, or cyclotetramethylene tetranitramine and further comprises a plasticizer that comprises n-butyl nitratoethyl nitramine, trimethylol ethane trinitrate, or triethyleneglycol dinitrate, wherein the propellant comprises about 4 weight % to about 10 weight % binder, about 45 weight % to about 75 weight % oxidizer, and about 6 weight % to about 18 weight % plasticizer.

6. The propellant of claim 1, wherein the oxidizer comprises ammonium perchlorate.

7. The propellant of claim 1, further comprising a plasticizer that comprises dioctyl adipate, or isodecyl pelargonate.

8. The propellant of claim 1, where in the oxidizer comprises ammonium perchlorate and further comprises a plasticizer that comprises n-butyl nitratoethyl nitramine, trimethylol ethane trinitrate, triethyleneglycol dinitrate, dioctyl adipate, or isodecyl pelargonate wherein the propellant comprises about 4 weight % to about 10 weight % binder, about 65 weight % to about 86 weight % oxidizer, and about 5 weight % to about 12 weight % plasticizer.

9. The propellant of claim 1, further comprising an aluminum or boron metal fuel.

10. The propellant of claim 1, wherein the oxidizer comprises ammonium perchlorate, ammonium nitrate, ammonium dinitramide, cyclotrimethylene trinitramide, or cyclotetramethylene tetranitramine and further comprises an aluminum or boron metal fuel and a plasticizer that comprises trimethylol ethane trinitrate, triethyleneglycol dinitrate, dioctyl adipate, or isodecyl pelargonate wherein the propellant comprises about 4 weight % to about 10 weight % binder, about 45 weight % to about 75 weight % oxidizer, about 15 weight % to about 24 weight % metal fuel and about 5 weight % to about 12 weight % plasticizer.

11. The propellant of claim 1, wherein the linear block co-polymer of caprolactone and tetramethylene ether binder has a melting range of about 86° F. to about 95° F.

* * * * *

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European Patent Office
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(54) Solid rocket propellant

(57) A solid rocket propellant includes a hydroxy-terminated caprolactone ether binder and an oxidizer. The propellant may be disposed of by contacting it with an aqueous solution of 12 N NaOH or 6 N HCl at a temperature of about 140°F (60°C) for about 24 hours to decompose the binder. Solids remaining in the solution after the binder decomposes are removed.

EP 1 069 095 A1

Description

[0001] The present invention is directed to a solid rocket propellant.

[0002] Solid rocket propellants typically comprise an oxidizer, a fuel, a variety of additives, and a binder that holds the propellant together. Typical oxidizers include ammonium nitrate, ammonium dinitramide, ammonium perchlorate, potassium perchlorate, and other compounds known in the art. Typical fuels include aluminum powder, boron, and beryllium. Typical binders include nitrocellulose, hydroxy terminated polybutadiene, butadiene terpolymer, polybutadiene-acrylic acid-acrylonitrile, carboxyl terminated polybutyldiene, polyesters, polyethylene glycol, poly tetramethylene glycol and other compounds known in the art. Typical additives include plasticizers such as n-butyl nitratoethyl nitramine, trimethylolethane trinitrate and isodecyl pelargonate, dioctyl adipate; burning rate modifiers such as iron oxide and carbon; combustion stabilizers such as zirconium oxide; anti-oxidants such as n-methyl nitroaniline and 2,2'-Methylene-Bis-(4-Methyl-6-Tert-Butylphenol) (available as AO-2246 from American Cyanamid Company, Parsippany, NJ); curing agents such as dimeryl diisocyante, isophorone diisocyanate, and Desmodur® N-100 (available from Bayer Corporation, Pittsburgh, PA); curing catalysts such as triphenyl bismuth and dibutyltin dilaurate; and acoustic suppressants such as silicon carbide.

[0003] Solid rocket propellants can be tailored to specific applications by varying their formulations. Although preliminary work on new formulations can be done in a laboratory with small quantities, testing and large scale demonstrations are typically required before a new formulation is accepted for military or commercial use. As a result, propellant development programs often generate considerable excess inventory of propellant. Production programs also generate excess inventory or off specification material. Finally, excess propellant is generated when rocket motors are periodically remanufactured to replace aging propellant with fresh propellant. In all cases, the excess inventory or off-specification material must be disposed of safely. Historically, open air incineration was the preferred disposal method. Increasingly, however, open air incineration is becoming environmentally unacceptable. Therefore, what is needed in the industry is a solid rocket propellant that can be disposed of with environmentally acceptable techniques.

[0004] The present invention is directed towards a solid rocket propellant that can be disposed of with environmentally acceptable techniques. As a side benefit, main components of the propellant can be recovered for reuse.

[0005] In accordance with one aspect of the invention there is provided a rocket motor propellant that includes a hydroxy-terminated caprolactone ether binder.

[0006] Another aspect of the invention includes a method of disposing of a solid rocket propellant. A solid rocket propellant that includes a hydroxy-terminated caprolactone ether binder and one or more solid compounds disposed in the binder is contacted with a solution capable of hydrolyzing the binder to form hydrolyzed caprolactone and poly(tetramethylene ether). Solids remaining in the solution after the binder hydrolyzes are removed.

[0007] These and other features and advantages of the present invention will become more apparent from the following description.

[0008] The present invention provides in its various embodiments a full range of solid rocket propellant formulations, including minimum smoke propellants, reduced smoke propellants, and metalized propellants. The common element in all aspects of the present invention is the use of a hydroxy-terminated caprolactone ether (HTCE) polymer as a binder to hold the solid constituents of the propellant of the present invention together. As a result, the propellant of the present invention comprises at least one solid compound, for example an oxidizer, dispersed in an HTCE binder. For purposes of this application, HTCE is a linear block co-polymer of caprolactone and tetramethylene ether. Preferably, HTCE will have a molecular weight of about 2000 units to about 4200 units. At typical HTCE may have an OH value of about 56 mg KOH/g, an acid value of less than about 0.1 mg KOH/g, and a melting range of about 86°F (30°C) to about 95°F (35°C). The preferred HTCE is a waxy solid at room temperature and is a liquid at typical propellant processing temperatures of 120°F (48.9°C) to 140°F (60°C). HTCE is commercially available from Solvay Interox, Inc. (Houston TX) as part of Solvay's CAPA® line of polycaprolactones. The HTCE binder may make up about 4 weight % to about 10 weight % of the propellant of the present invention.

[0009] Minimum smoke propellants of the present invention include an HTCE binder and a chlorine-free oxidizer. Suitable chlorine-free oxidizers include ammonium nitrate (AN), ammonium dinitramide (ADN), nitramines such as cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX), and other chlorine-free oxidizers known in the art. A minimum smoke propellant may comprise about 45 weight % to about 75 weight % of the oxidizer. If desired, the propellant also may include one or more nitrate ester plasticizers such as n-butyl nitratoethyl nitramine (BuNENA), trimethylol ethane trinitrate (TMETN), triethylene glycol dinitrate (TEGDN), and other nitrate ester plasticizers known in the art for additional energy. Plasticizers may make up about 6 weight % to about 18 weight % the minimum smoke propellant. Minimum smoke propellants of the present invention may have a theoretical specific impulse of more than 230 lb_f sec/lb_m (2255 N sec/kg) with an AN oxidizer and more than 260 lb_f sec/lb_m (2550 N sec/kg) with an ADN oxidizer. Such propellants may be useful in tactical applications where a visible exhaust is undesirable because it would expose a rocket's firing position.

[0010] Reduced smoke propellants of the present invention include an HTCE binder and a chlorinated oxidizer.

Suitable chlorinated oxidizers include ammonium perchlorate (AP), which may make up about 65 weight % to about 86 weight % of a reduced smoke propellant. If desired, the propellant also may include one or more energetic plasticizers such as BuNENA, TMETN, and TEGDN or fuel plasticizers such as dioctyl adipate (DOA) or isodecyl pelargonate (IDP). Plasticizers may make up about 5 weight % to about 12 weight % of the reduced smoke propellant. Reduced smoke propellants of the present invention may have a theoretical specific impulse of more than 244 lb_f sec/lb_m (2393 N sec/kg) with an AP oxidizer. Such propellants may be useful in tactical applications, such a air-to-air applications, where a small amount of visible exhaust is tolerable as long as the exhaust does not obscure an operator's field of view.

[0011] Metalized propellants of the present invention include an HTCE binder, metal fuel, and an oxidizer. Suitable metal fuels include aluminum, boron, and other metal fuels known in the art. The preferred metal fuel is aluminum. The metal fuel may make up about 15 weight % to about 24 weight % of the metalized propellant. Suitable oxidizers include AP, AN, ADN, HMX, RDX, and other oxidizers known in the art. The oxidizer may make up about 45 weight % to about 75 weight % of the metalized propellant. If desired, the propellant also may include one or more energetic plasticizers, such as TMETN or TDGDN, or fuel plasticizers, such as DOA or IDP. Plasticizers may make up about 5 weight % to about 12 weight % of metalized propellants of the present invention. Metalized propellants of the present invention may have a theoretical specific impulse of more 263 lb_f sec/lb_m (2579 N sec/kg) with AP oxidizer and 268 lb_f sec/lb_m (2628 N sec/kg) with ADN or HMX oxidizer. Such propellants may be useful in applications for which high energy content is desirable and for which visible exhaust is not a problem.

[0012] The HTCE binder of the present invention can be cured with a variety of curing agents including di-functional isocyanates such as isophorene diisocyante (IPDI), dimeryl diisocyanate (DDI), bis-(4,isocyanatocyclohexyl) methane (Desmodur®-W, available from Bayer Corporation, Pittsburgh, PA), and other di-functional isocyanates; and poly-functional isocyanates such as aliphatic isocyanates made by the homo-polymerization of hexamethylene diisocyanate, including Desmodur® N-100 and Desmodur® N-3200 (both available from Bayer Corporation), and other poly-functional isocyanates. The curing agent may make up as much as about 2.75 weight % of the propellant. A cross-linker may be desirable when di-functional isocyanates are use as curing agents. Preferable cross-linkers include tri-functional and tetra-functional hydroxy terminated caprolactones, such as CAPA® 310 and CAPA® 316 (available from Solvay Interox, Inc.). The cross-linker may make up as much as about 2.0 weight % of the propellant of the present invention. A cure catalyst such as triphenyl bismuth (TPB), dibutyltin dilaurate (DBTDL), or similar cure catalysts may be used to speed the cure reaction. Typical amounts of TPB in the propellant range from about 0.01 weight % to about 0.05 weight %. Typical amounts of DBTDL range from about 1 PPM by weight to about 6 PPM by weight. HTCE may be cured under conditions typically used in the industry. For example, HTCE may be cured at temperatures of about 120°F (49°C) to about 140°F (60°C) for times ranging from 3 days to 2 weeks.

[0013] The propellant of the present invention also may include stabilizers, acoustic suppressants, burner rate modifiers, and other additives. For example, propellants of the present invention may include up to about 0.5 weight % of one or more stabilizers, such as N-methyl-*p*-nitroanaline (NMNA), 2-nitro diphenylamine (NDPA), or other stabilizers known in the art, to extend their useful lives. Stabilizers may be particularly useful in propellants that contain nitrate ester plasticizers. The propellants also may include up to about 0.5 weight % of an acoustic suppressants such as silicon carbide or zirconium carbide. Burn rate modifiers, such as carbon black and/or lead compounds including lead citrate, may be included in the propellant of the present invention in amounts up to about 0.2 weight %. Iron oxide can be used as a burning rate modifier in formulations without energetic nitrate ester plasticizers in amounts up to about 2 weight %.

[0014] By varying the formulation, burn rates for the propellant of the present invention may be tailored for numerous applications. Burning rates have been observed as low as 0.18 in/sec (0.46 cm/sec) and as high as 0.34 in/sec (0.86 cm/sec) at 1000 psi (6895 kPa) for formulations without any burning rate modifiers. Pressure exponents were between 0.3 and 0.4. The ranges of burning rates and pressure exponents may be expanded by using various additives and curing catalysts discussed above. It should be possible to formulate metalized propellants with iron oxide burning rate catalyst that have burning rates as high as 0.75 in/sec (1.91 cm/sec) at 1000 psi (6895 kPa).

[0015] The mechanical properties of the HTCE binder, such as modulus, tensile strength, and elongation, also may be tailored for particular applications. For example, the modulus may be varied from about 300 psi (2068 kPa) to about 700 psi (4826 kPa), the tensile strength may be varied from about 75 psi (517 kPa) to about 150 psi (1034 kPa), and the elongation may be varied from about 30% to about 150% of the propellant of the present invention. One way to adjust the mechanical properties of the binder is to vary the isocyanate/hydroxyl (NCO/OH) equivalent ratio. For example, the NCO/OH equivalent ratio may be varied from about 0.95 to about 1.20. Another method is to add about 0.1 weight % to about 2.0 weight % of a tri-functional or tetra-functional hydroxyl-terminated caprolactone to the formulation as a cross-linker in the propellant. The cross-linker promotes cross-linking within the HTCE co-polymer structure. Suitable cross-linkers include tri-functional and tetra-functional hydroxy terminated caprolactones, such as CAPA® 310 and CAPA® 316 (available from Solvay Interox, Inc.).

[0016] Once a specific formulation is chosen, the ingredients are mixed in an explosion proof mixing vessel according to industry practices to create an uncured propellant. The uncured propellant may be loaded into a rocket casing or

other container by known casting techniques and cured under suitable conditions. For example, the propellant of the present invention may be cured at temperatures of about 120°F (49°C) to about 140°F (60°C). It may take about 3 days to about 14 days to cure a batch of propellant of the present invention. Samples of the cured propellant may then be tested to confirm the properties. The final product would then be ready to deliver to the customer.

[0017] Over time, quantities of propellant that require disposal may be accumulated as a result of off-specification mixing, excess production, natural degradation of the propellant, obsolescent propellant or missiles being removed from service, and similar events. In the past, such propellant was typically disposed of by open air incineration. Propellants of the present invention, however, may be disposed of by hydrolyzing the HTCE binders in the propellant. The ester linkage in the caprolactone in the HTCE binder provides the site for hydrolysis. The polyether linkage in the HTCE binders increase the hydrophilicity of the cured binder toward aqueous acidic and/or basic solutions. Thus, the polyether linkage is more resistant to hydrolysis than the ester linkage.

[0018] To dispose of propellant of the present invention by hydrolysis, the propellant may be reduced in size to facilitate handing and increase surface area for the reaction. While no particular size reduction is required, preferably the propellant will be reduced to pieces of no more than about 0.5 inch (1.3 cm) in any dimension. The propellant is then mixed with a solution capable of hydrolyzing HTCE. For example, HTCE may be hydrolized in an acidic aqueous solution of 6 N HCl (hydrochloric acid) or a basic aqueous solution of 12 N NaOH (sodium hydroxide). One skilled in the art will recognize that solutions with different compositions and concentrations would work as well. Preferable, the hydrolysis will be conducted at an elevated temperature, for example about 140°F (60°C), for a sufficient time to completely hydrolyze the HTCE. Agitation can speed the hydrolysis reaction. By selecting appropriate conditions, hydrolysis can be completed within about 24 hours. As a result of the hydrolysis reaction, the HTCE binder will decompose into water soluble, environmentally benign compounds such as hydrolyzed caprolactone, typically ω-hydroxyl caproic acid, and poly(tetramethylene ether) that may be recycled. Solids that were in the propellant, for example the oxidizer and other solids, may be recovered and recycled for use in other propellants. Aluminum may be recovered as aluminum oxide. The ability to recover and reuse the solids, which may make up 85 weight % or more of the propellant, greatly reduces the environmental impact of disposing of propellants of the present invention. The residue of hydrolysis that cannot be recycled may be disposed of in a suitable landfill without any environmental harm.

[0019] The following examples demonstrates the present invention without limiting the invention's broad scope.

Example 1

[0020] To demonstrate the present invention, several propellants were formulated using a HTCE binder. The table shows the compositions, mechanical properties, and where available burning rate and pressure exponent data.

Table

	Propellant A Metalized	Propellant B Metalized	Propellant C Reduced Smoke
HTCE binder (MW = 2000)	8.80	4.21	6.21
CAPA® 316 cross-linking agent	0.18	1.05	1.04
Diocytal adipate (DOA) plasticizer	4.84		
n-butyl nitratoethyl nitramine (BuNENA) plasticizer		15.54	10.65
n-methyl nitroanaline (NMNA) stabilizer		0.50	0.50
triphenyl bismuth (TPB) cure catalyst	0.05	0.05	0.05
silicon carbine (SiC) acoustic suppressant			0.50
carbon (C) black burning rate modifier			0.20
dimeryl diisocyante (DDI) curing agent	3.13	2.50	3.40

Table (continued)

	Propellant A Metalized	Propellant B Metalized	Propellant C Reduced Smoke
ammonium perchlorate (AP) oxidizer	63.00	56.00	77.20
aluminum (Al) fuel	20.00	20.00	
modulus, psi (kPa)	623 (4295)	100 (689)	383 (2641)
tensile strength, psi (kPa)	92 (634)	29 (200)	45 (310)
elongation, failure %	65	43	20
burning rate, in/sec @ 1000 psi (cm/sec @ 6895 kPa)		0.28 (0.71)	0.26 (0.66)
pressure exponent		0.39	0.36

Example 2

[0021] A 2.0-gram sample of cured HTCE gum stock was cut into small pieces of no more than 0.5 inch (1.3 cm) in any dimension. The cut pieces were placed in a beaker containing 50-ml of 12 N NaOH aqueous solution. The solution was stirred with a magnetic stirrer and heated on a hot plate. The reaction temperature was kept at 60°C. At the end of reaction, about 24 hours, all solid gum stock dissolved and some oil droplet suspension was visible. These results indicate that the HTCE binder may be hydrolyzed as part of a method of disposing of a propellant of the present invention.

[0022] The invention is not limited to the particular embodiments shown and described herein. Various changes and modifications may be made without departing from the spirit or scope of the claimed invention.

Claims

1. A rocket motor propellant comprising a hydroxy-terminated caprolactone ether binder and an oxidizer.

2. The propellant of claim 1, wherein the hydroxy-terminated caprolactone ether is a linear block co-polymer of caprolactone and tetramethylene ether.

3. The propellant of claim 1 or claim 2, wherein the hydroxy-terminated caprolactone ether has a molecular weight of about 2000 to about 4200 units.

4. The propellant of any one of claims 1 to 3, wherein the oxidizer comprises ammonium nitrate, ammonium dinitramide, cyclotrimethylene trinitramide, cyclotetramethylene tetranitramine or ammonium perchlorate.

5. The propellant of any one of claims 1 to 4, further comprising a plasticizer that comprises n-butyl nitratoethyl nitramine, trimethylol ethane trinitrate, triethyleneglycol dinitrate, dioctyl adipate or isodecyl pelargonate.

6. The propellant of any one of claims 1 to 5, further comprising an aluminum or boron metal fuel.

7. The propellant of any one of claims 1 to 3, wherein the oxidizer comprises ammonium nitrate, ammonium dinitramide, cyclotrimethylene trinitramide, or cyclotetramethylene tetranitramine and further comprises a plasticizer that comprises n-butyl nitratoethyl nitramine, trimethylol ethane trinitrate, or triethyleneglycol dinitrate, wherein the propellant comprises about 4 weight % to about 10 weight % HTCE binder, about 45 weight % to about 75 weight % oxidizer, and about 6 weight % to about 18 weight % plasticizer.

8. The propellant of any one of claims 1 to 3, wherein the oxidizer comprises ammonium perchlorate and further comprises a plasticizer that comprises n-butyl nitratoethyl nitramine, trimethylol ethane trinitrate, triethyleneglycol dinitrate, dioctyl adipate, or isodecyl pelargonate wherein the propellant comprises about 4 weight % to about 10 weight % HTCE binder, about 65 weight % to about 86 weight % oxidizer, and about 5 weight % to about 12 weight % plasticizer.

9. The propellant of any one of claims 1 to 3, wherein the oxidizer comprises ammonium perchlorate, ammonium

nitrate, ammonium dinitramide, cyclotrimethylene trinitramide, or cyclotetramethylene tetranitramine and further comprises an aluminum or boron metal fuel and a plasticizer that comprises trimethylol ethane trinitrate, triethyleneglycol dinitrate, dioctyl adipate, or isodecyl pelargonate wherein the propellant comprises about 4 weight % to about 10 weight % HTCE binder, about 45 weight % to about 75 weight % oxidizer, about 15 weight % to about 24 weight % metal fuel and about 5 weight % to about 12 weight % plasticizer.

10. A method of disposing of a solid rocket propellant, comprising the steps of:

(a) contacting a propellant that comprises a hydroxy-terminated caprolactone ether binder and at least one or more solid compounds dispersed in the binder with a solution capable of hydrolyzing the binder to form hydrolyzed caprolactone and poly(tetramethylene ether), and
(b) removing solids remaining in the solution after the binder hydrolyzes.

11. The method of claim 10, wherein the solids are recovered and recycled.

12. The method of claim 10 or claim 11, wherein the hydrolyzed caprolactone and the poly(tetramethylene ether) binder ingredients are recovered and recycled.

13. The method of any one of claims 10 to 12, wherein the propellant is as claimed in any one of claims 1 to 9.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 5886

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 266 973 A (MORTON THIOKOL, INC.) 11 May 1988 (1988-05-11) * page 3, line 45 - line 49; claims *	1,3-9	C06B45/10 C06B21/00
X	US 5 240 523 A (R.L. WILLER) 31 August 1993 (1993-08-31) * claims; example 3 *	1,4-9	
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A	DE 195 20 548 A (M. BOHN) 12 December 1996 (1996-12-12) * claims *	10-13	
A	US 4 098 627 A (A.S. TOMPA ET AL.) 4 July 1978 (1978-07-04) * claims *	10-13	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C06B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 October 2000	Schut, R

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 5886

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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